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COMPLEXES OF LIGANDS CONTAINING PHENYL AND CYCLOPENTADIENYL RINGS. SYNTHESIS, CHARACTERIZATION AND SPECTROSCOPIC STUDIES ON TRICARBONYLMANGANESE DERIVATIVES*

NIALL J. GOGAN* and CHIT-KAY CHU**

Department of Chemistry, Memorial University of Newfoundland, St. John's, Newfoundland (Canada)

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Summary

A series of (benzoylcyclopentadienyl)manganese tricarbonyl derivatives have been prepared and characterized. In addition several other $Mn(CO)_3$ complexes containing both a phenyl and a cyclopentadienyl ring have been prepared and characterized including the benzylcyclopentadienyl, phenylcyclopentadienyl and styrylcyclopentadienyl complexes. They have been studied by UV, IR and proton NMR. The ketonic $\nu(CO)$ is significantly affected by *o*- or α-substitution. Shifts in τ values in the proton NMR spectra on substitution are interpreted in terms of both electronic and steric effects.

Introduction

Complexes containing two or more metal atoms bonded to one ligand molecule, without metal—metal bonds, have been of continuing interest in this laboratory [1-4]. The main interest in these compounds is the elucidation of the effect transmitted through the ligand of one metal on the other. A thorough study of such effects has been impeded by difficulties in preparing an extensive series of compounds [4] or by the absence of significant transmitted effects [3]. A previous paper from this laboratory [5] showed by an ESR study that (benzoylcyclopentadienyl)manganese tricarbonyls are amenable to such studies. Work was then started to prepare an extensive series of these compounds. This paper describes the first part of this work which is the preparation, characterization and spectroscopic study of substituted (benzoylcyclopentadienyl)manganese tricarbonyls and other similar compounds containing a phenyl and a cyclopenta-

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* Taken from the Ph.D. thesis of Chit-Kay Chu, Memorial University of Newfoundland, 1974.

** Present address: Department of Chemistry, University of Malaya, Kuala Lumpur, Malaysia.

dienyl ring. Subsequent papers will describe corresponding mixed tricarbonylchromium—tricarbonylmanganese complexes and various studies on these including the ESR study of their anions. In all of these studies, more emphasis will be placed on the ketones than on the others because of the increased probability of conjugation and the relative ease of formation of anions.

Experimental

All the preparations were carried out in an atmosphere of dry purified nitrogen. All solvents used in preparations and recrystallizations were dried and distilled in an atmosphere of nitrogen before use. Melting points were obtained using a Fisher-Johns block apparatus and are reported uncorrected. The C, H and halogen analyses were performed by either Beller or Alfred Bernhardt Laboratories, West Germany. Metal analyses were carried out using a Varian AA-5 atomic absorption spectrometer. Percentage yields are based on the metal—ligand carbonyls used.

The IR spectra were recorded on a Perkin—Elmer 457 spectrometer in spectrograde carbon tetrachloride solution using a 1 mm fixed path-length cell with sodium chloride windows. Regions above 2,000 cm^{-1} were calibrated against the 2143.2 cm^{-1} band of CO, those between 2,000 and 1,800 cm^{-1} against DCl while regions below 1,800 cm^{-1} were calibrated against polystyrene. Scale-expansion (X 2.5) was used in measuring regions above 1600 cm^{-1}. All the spectra could be reproduced to within ± 1 cm^{-1}. Spectra of Nujol mulls were recorded using KBr plates. The intensities quoted in the tables are relative to the most intense band. The following notations are used, weak (w), medium (m), strong (s), very strong (vs), and shoulder (sh).

Mass spectra were recorded on a Hitachi—Perkin—Elmer RMU-6E spectrometer. UV spectra were recorded on a Unicam SP800 spectrometer using spectrograde hexane and 1 cm quartz cells. The bands were calibrated with holmium oxide bands.

Proton NMR spectra were recorded with a Varian HA100 spectrometer in $CDCl_3$ solutions, using TMS as an internal reference and locking signal.

Preparations

The preparation of (benzoylcyclopentadienyl)manganese tricarbonyl and its α- and β-methyl derivatives have been reported earlier [5]. The other ketones were prepared by the same method and their m.p.'s and elemental analyses are given in Table 1. In some instances, the α- and β-methyl isomers were separated by fractional recrystallization, whereas in other cases column chromatography had to be used. In some cases, distillation under reduced pressure was used.

(Benzylcyclopentadienyl)manganese tricarbonyl ketone, $C_6H_5CH_2COC_5H_4Mn(CO)_3$. This was prepared by Friedel—Crafts Acylation. Purification was achieved by the chromatographic method using a 70/30 mixture of hexane/ CH_2Cl_2 as eluant and alumina as the stationary phase. The yellow fraction obtained was micro-distilled and the viscous orange distillate crystallised on the cold-finger. Yield 60%, m.p. 59°C. (Found: C, 60.02; H, 3.52; Mn, 17.61. $C_{16}H_{11}O_4Mn$ calcd.: C, 59.64; H, 3.44; Mn, 17.06%.)

(Benzylcyclopentadienyl)manganese tricarbonyl carbinol, $C_6H_5CH_2CH$-

TABLE 1. ELEMENTAL ANALYSES AND M.P.'S OF $XC_6H_4COC_5H_3(Y)Mn(CO)_3$

Compound		M.p. (°C)	Analysis found (calcd.) (%)			
X	Y		C	H	Mn	Hal[a]
H	H	73-74	58.28	2.89	18.02	
			(58.46)	(2.94)	(17.83)	
H	α-CH_3	118-119	59.71	3.39	17.60	
			(59.64)	(3.44)	(17.06)	
H	β-CH_3	54-55	59.85	3.53	17.62	
			(59.64)	(3.44)	(17.06)	
o-CH_3	H	108	59.80	2.88	17.50	
			(59.64)	(3.44)	(17.06)	
o-CH_3	α-CH_3	69-70	60.82	3.98	16.58	
			(60.73)	(3.90)	(16.35)	
o-CH_3	β-CH_3	oil	60.90	3.68	16.40	
			(60.73)	(3.90)	(16.35)	
m-CH_3	H	50	60.04	3.40	17.13	
			(59.64)	(3.44)	(17.06)	
m-CH_3	β-CH_3	66-67	60.66	3.86	16.03	
			(60.73)	(3.90)	(16.35)	
p-CH_3	H	97	59.56	3.08	17.21	
			(59.64)	(3.44)	(17.06)	
p-CH_3	α-CH_3	96-97	61.00	3.87	16.21	
			(60.73)	(3.90)	(16.35)	
p-CH_3	β-CH_3	85	60.73	3.97	16.56	
			(60.73)	(3.90)	(16.35)	
o-Cl	H	103-104	52.44	2.60	15.96	11.00
			(52.58)	(2.34)	(16.03)	(10.36)
o-Cl	α-CH_3	104-105	53.42	2.91	15.70	10.11
			(53.88)	(2.83)	(15.41)	(9.95)
o-Cl	β-CH_3	70-71	53.18	2.94	15.76	10.33
			(53.88)	(2.83)	(15.41)	(9.95)
p-Cl	H	85-86	53.05	2.36	15.92	10.49
			(52.58)	(2.34)	(16.03)	(10.36)
p-Cl	α-CH_3	72	53.56	2.96	14.98	10.01
			(53.88)	(2.83)	(15.41)	(9.95)
p-Cl	β-CH_3	95	53.32	3.03	15.90	10.28
			(53.88)	(2.83)	(15.41)	(9.95)
o-F	H	112	55.44	2.45	16.28	5.8
			(55.24)	(2.47)	(16.84)	(5.83)
m-F	H	75	55.41	2.81	17.10	5.8
			(55.24)	(2.47)	(16.84)	(5.83)
m-F	α-CH_3	113	56.28	2.75	16.50	5.8
			(56.49)	(2.96)	(16.15)	(5.59)
p-F	H	65	54.95	2.39	16.64	6.4
			(55.24)	(2.47)	(16.84)	(5.83)
p-F	β-CH_3	67	55.88	2.98	16.30	5.8
			(56.49)	(2.96)	(16.15)	(5.59)
p-OCH_3	H	92	56.91	3.44	16.17	
			(56.82)	(3.28)	(16.25)	
p-OCH_3	α-CH_3	103-104	57.25	3.85	16.00	
			(57.97)	(3.72)	(15.60)	
p-OCH_3	β-CH_3	79-80	56.88	3.83	15.90	
			(57.97)	(3.72)	(15.60)	

[a] Hal is Cl or F.

$(OH)C_5H_4Mn(CO)_3$. A solution of $C_6H_5CH_2COC_5H_4Mn(CO)_3$ (0.5 g, 1.6 mmol) in 20 ml of absolute methanol was kept at 20°C. A solution of sodium borohydride (0.2 g, 5.3 mmol) in 2 ml of 5% NaOH was then slowly stirred into the

reaction flask and the mixture was stirred in a cold bath for 2 h. A small amount of the mixture was pipetted out and tested with dilute acid to ensure excess of borohydride. The methanol was distilled off and the resulting yellow solid was redissolved in diethyl ether. The ethereal solution was washed several times with water, dried over anhydrous $CaCl_2$ and the ether removed. A light yellow solid was obtained which was recrystallised from hot hexane. Yield 0.18 g (90%), m.p. 97°C.(Found: C, 59.70; H, 3.98; Mn, 17.06. $C_{16}H_{13}O_4Mn$ calcd.: C, 59.27; H, 4.04; Mn, 16.95%.)

(Styrylcyclopentadienyl)manganese tricarbonyl, $C_6H_5CH{=}CHC_5H_4Mn(CO)_3$. The freshly prepared $C_6H_5CH_2CH(OH)C_5H_4Mn(CO)_3$ (0.4 g, 1 mmol) was mixed with $KHSO_4$ (0.2 g, 1.5 mmol) and a pinch of hydroquinone as catalyst. The mixture was heated in a stoppered flask equipped with a cold-finger at a temperature of —170-175°C for 2 h. Droplets of water condensed on the cold-finger. The residue was then micro-distilled and the distillate was collected at 100°C/0.5 Torr. The distillate solidified when disturbed. Yield 0.31 g (82%), m.p. 97-98°C. (Found: C, 62.66; H, 3.73; Mn, 18.02. $C_{16}H_{11}O_3Mn$ calcd.: C, 62.76; H, 3.63; Mn, 17.95%.)

(Benzyl-α-methylcyclopentadienyl)manganese tricarbonyl, $C_6H_5CH_2(\alpha\text{-}CH_3)C_5H_3Mn(CO)_3$. A 1/1 mixture of $LiAlH_4$ (0.12 g, 3 mmol) and $AlCl_3$ (0.44 g, 3 mmol) in sodium-dried-ether was treated dropwise with an ethereal solution of $C_6H_5CO(\alpha\text{-}CH_3)C_5H_3Mn(CO)_3$ (1 g, 3 mmol). Brisk effervescence was observed and the solution turned from yellow to light red. The mixture was then refluxed for 3 h, cooled in an ice-bath and then treated with water added dropwise. The ethereal layer was washed with a 5% solution of $NaHCO_3$ followed by water and then dried over anhydrous $MgSO_4$. The ether was removed on a rotatory evaporator and a viscous yellow oil was obtained. The oil was chromatographed with a 1/1 mixture of heptane/benzene through neutral alumina and two fractions were obtained. The first fraction was micro-distilled and the golden-yellow distillate was collected at 110°C/1 Torr. Yield 0.7 g (76%). The second fraction was found to be the starting material. IR and PMR spectra confirmed the complete reduction of the ketonic carbonyl to the methylene group. (Found: C, 62.50; H, 4.06; Mn, 18.01. $C_{16}H_{13}O_3Mn$ calcd.: C, 62.35; H, 4.25; Mn, 17.83%.)

(Benzyl-β-methylcyclopentadienyl)manganese tricarbonyl, $C_6H_5CH_2(\beta\text{-}CH_3)C_5H_3Mn(CO)_3$. The procedure was the same as that used for the α-isomer. The product was collected at 70°C/1 Torr. Yield 70%.

(Benzylcyclopentadienyl)manganese tricarbonyl, $C_6H_5CH_2C_5H_4Mn(CO)_3$. The reduction procedure was similar to that previously described. The product was collected as a golden-yellow oil at 80°/0.2 Torr which solidified when disturbed mechanically. Yield 72%, m.p. 38°C. (Found: C, 60.98; H, 3.70; Mn, 18.93. $C_{15}H_{11}O_3Mn$ calcd.: C, 61.24; H, 3.77; Mn, 18.68%.)

(Pentadeuteriobenzoylcyclopentadienyl)manganese tricarbonyl, $C_6D_5COC_5H_4Mn(CO)_3$. A solution of C_6D_5Br (Merck, Sharp and Dohme) (20 g, 120 mmol) was dissolved in 20 ml of anhydrous ether and slowly added to some magnesium turnings (3 g, 130 mmol). The Grignard reaction was initiated and allowed to proceed until all the C_6D_5Br had been added. The mixture was refluxed for another hour. It was then poured into a beaker of solid CO_2 followed by 250 ml of 1/1 HCl solution which were slowly stirred into the thick slurry. The benzoic

acid was precipitated out of solution with a 1/1 HCl solution. The resulting solution was filtered and dried over P_2O_5. Yield 11.5 g (76%). The NMR spectrum of this compound showed no indication of deuterium exchange.

The deuterated benzoic acid was treated with redistilled $SOCl_2$ (15 g, 120 mmol) in the presence of a trace of DMF and CuCl acting as a polymerisation inhibitor [6]. The mixture was placed over a hot water bath until no HCl or SO_2 was given off. Excess $SOCl_2$ was distilled off and the C_6D_5COCl was collected at 100°C/40 Torr. Yield 10.8 g (95%). The NMR spectrum confirmed the structure; no aromatic proton resonance was observed.

The C_6D_5COCl was then treated with $C_5H_5Mn(CO)_3$ and $AlCl_3$ as previously described in the Friedel—Crafts method of preparation. Yield 56%, m.p. 134-135°C.

(Pentadeuteriobenzoylmethylcyclopentadienyl)manganese tricarbonyl, $C_6D_5CO(CH_3)C_5H_3Mn(CO)_3$. The preparation was carried out using the Friedel—Crafts procedure. The α- and β-isomers were isolated by fractional recrystallisation. NMR and mass spectral analyses showed no detectable deuterium exchange. Overall yield 65%. α-isomer m.p. 121°; β-isomer m.p. 59-60°C.

(Phenylcyclopentadienyl)magnagese tricarbonyl, $C_6H_5C_5H_4Mn(CO)_3$. Phenyllithium was prepared by treating freshly cut lithium metal (1.5 g, 100 mmol) in diethyl ether with bromobenzene (17.5 g, 100 mmol). The reaction was completed in 1 h. The mixture was cooled and filtered on a vacuum line using Kontes "Airless ware apparatus". A solution of 2-cyclopentene-1-one (5 g, 60 mmol) in 20 ml ether was slowly introduced into the phenyllithium solution and the mixture stirred in an ice-bath for four hours. It was then poured into a beaker of ice cold water and the ethereal layer washed and dried over anhydrous $CaCl_2$. The ether was removed. The viscous oil obtained was dehydrated by blowing a stream of nitrogen over it at a temperature of about 180°C. The dark yellow oil was distilled at 60-65°C/0.3 Torr and the clear distillate solidified as a white solid on the walls of the condenser. This solid readily changed to a light yellow oil on standing and had to be redistilled. Yield 3.3 g, (40%), m.p. 47°C. The mass spectrum showed the molecular ion at m/e 142. The NMR spectrum showed peaks at τ 6.7, τ 3.5, τ 3.2 and τ 2.8 ppm which agreed with that expected for monomeric $C_6H_5C_5H_5$.

The freshly prepared $C_6H_5C_5H_5$ (2.8 g, 10 mmol) was dissolved in 10 ml of THF and added slowly into dispersed sodium (0.46 g, 20 mmol) in THF. The mixture was refluxed for 1 h, cooled and the solution of $Mn(CO)_5Br$ (2.7 g, 10 mmol) in THF was added dropwise. It was then refluxed for another 2 h. The excess sodium was destroyed using aqueous pet. ether (30-60°). The ethereal layer was washed several times with water and dried over anhydrous $CaCl_2$. The ether was removed and the resulting viscous oil distilled. Clear golden-yellow oil droplets were collected at 65-70°C/0.3 Torr. Yield 0.84 g (40%). (Found: C, 60.84; H, 3.41; Mn, 19.71. $C_{14}H_9O_3Mn$ calcd.: C, 60.02; H, 3.24; Mn, 19.63%.)

Results and discussion

Synthesis and characterization

The ketones were prepared by Friedel—Crafts benzoylation [7]:

$$XC_6H_4COCl + YC_5H_4Mn(CO)_3 \xrightarrow[CH_2Cl_2]{AlCl_3} XC_6H_4CO(Y)C_5H_3Mn(CO)_3$$

In this reaction X is H, CH_3, OCH_3, Cl or F and Y is H or CH_3. (See Table 1 for a complete listing.) The *o*-hydroxy compound was obtained during the attempted preparation of the *o*-methoxy compound. These compounds are fairly stable in the solid state to air but readily decompose in the liquid state or in solution. They are mostly light yellow in color and often form oils which are difficult to crystallize. The benzyl compounds were prepared by reduction of the corresponding benzoyl compounds using lithium aluminum hydride/ aluminum chloride in ether.

The styryl compound was prepared in a three step reaction sequence. The ketone $C_6H_5CH_2COC_5H_4Mn(CO)_3$ was prepared by the usual method and then reduced to the alcohol by sodium borohydride in methanol. The hydroxy compound was converted to the styryl compound by eliminating water in the presence of $KHSO_4$/hydroquinone.

(Phenylcyclopentadienyl)manganese tricarbonyl was prepared by reacting the sodium salt of phenylcyclopentadiene [8] with bromomanganese pentacarbonyl.

In each case the empirical formula was confirmed by elemental analysis. The presence of the $Mn(CO)_3$ group was verified by the observation of the A_1 and E $\nu(CO)$ bands in the IR, the E band being slightly split. The characteristic ketone $\nu(CO)$ was observed for all the ketones. The structures assigned were confirmed by observations of the expected NMR spectra. The isomers were also distinguished by this method.

Infrared spectra

The carbonyl stretching frequencies of both the $Mn(CO)_3$ and ketonic groups are given in Table 2. Those of the $Mn(CO)_3$ are designated A_1 and E for convenience even though the local symmetry has not always C_{3v} symmetry. When the cyclopentadienyl ring is substituted with a methyl group there is a general decrease in the $\nu(CO)$ of the $Mn(CO)_3$ moiety. Though this decrease

TABLE 2

CARBONYL STRETCHING FREQUENCIES OF SOME $XC_6H_4COC_5H_3(Y)Mn(CO)_3$ COMPOUNDS (cm^{-1}) IN CCl_4 SOLUTION

	Y = H			Y = α-CH_3			Y = β-CH_3		
X	A_1	E	Ketonic	A_1	E	Ketonic	A_1	E	Ketonic
H	2034	1962, 1953	1661	2029	1953, 1949	1659	2030	1954, 1945	1659
o-CH_3	2034	1960, 1952	1665	2030	1952, 1949	1662	2031	1957, 1947	1665
m-CH_3	2032	1956, 1950	1655	2031	1951, 1947	1653	2029	1955, 1946	1655
p-CH_3	2033	1959, 1948	1655	2033	1953, 1948	1656	2030	1957, 1944	1655
p-OCH_3	2034	1959, 1947	1649	2029	1953, 1946	1650	2030	1955, 1946	1648
o-Cl	2034	1958, 1952	1673	2031	1948, 1950	1663	2031	1955, 1947	1669
p-Cl	2031	1961, 1952	1657	2029	1955, 1950	1660	2028	1959, 1948	1656
o-F	2032	1963, 1954	1666						
m-F	2032	1960, 1951	1660	2030	1954, 1951	1660			
p-F	2034	1960, 1951	1656				2028	1955, 1946	1655

is small, it is nevertheless consistently recurring. This is in agreement with simple molecular orbital theory as discussed by Brown and Sloan [9].

It is also seen from Table 2 that substituents on the phenyl rings are too remote to have any significant effect on the $Mn(CO)_3$ moiety. Only a random change in the C—O stretching vibrations is observed. This does not imply that the two ring systems are not conjugated but only that the conjugation is not strong in contrast to biphenyl or phenanthrene derivatives [10] where the ring systems are directly linked to each other and substituent changes on one ring effect the C—O vibrations of the $M(CO)_3$ complexed to the other.

The loss of degeneracy of the E mode, as indicated by the splitting of this mode into a doublet, is not altogether unexpected for such a large molecule. This supports the view of Adams and Squire [11] that the C_{3v} local symmetry approximation for an $M(CO)_3$ group is inadequate if there are significant interactions between the ring and the C_{3v} site. This splitting is not very obvious in solution spectra of non-ketonic complexes (Table 3). It does appear that the ketonic carbonyl is mainly responsible for such a loss of C_{3v} symmetry.

The stretching frequencies of the ketonic carbonyl group often reveal much information about the electronic effects of the system. Though several workers [12] have discussed the vibrational frequencies of ketonic carbonyls it is not possible to associate such studies solely with electron distributions about the C—O bond. The frequency shifts of ν(CO) have been interpreted in terms of induction resonance, field effects, changes in the hybridisation with bond angle and in terms of energy associated with stretching and bonding force constants of the C—X and C—Y bonds in the ketones XCOY. It is not possible to measure the bond force constant of the ketonic carbonyl in such large molecules as described here because many factors which may contribute to this effect are involved. Only a comparative study of the ν(CO) frequencies will be attempted.

It is seen from Table 2 that a methyl substituent on the cyclopentadienyl ring does not seem to affect the ketonic carbonyl frequency as much as if it was on the phenyl ring. When the substitution is at the *ortho* position of the phenyl ring a comparatively higher ν(CO) is observed whereas substitution of the methyl group at the α-position appears to show a slight decrease in ν(CO). The $-C_5H_4Mn(CO)_3$ group may be considered to have a mainly inductive effect and the electronic effects may be visualised as in Fig. 1. Structure b de-

TABLE 3

ν(CO) OF $RC_5H_4Mn(CO)_3$ (cm^{-1}) IN CCl_4 SOLUTION

R	ν(CO) of $Mn(CO)_3$	
	A_1	E
H	2028	1945
CH_3	2024	1942
C_6H_5	2025	1941
$C_6H_5CH_2$	2024	1938
$C_6H_5CH_2CO$	2034	1958, 1949
$C_6H_5CH_2CH(OH)$	2026	1940
$C_6H_6CH{=}CH$	2022	1942

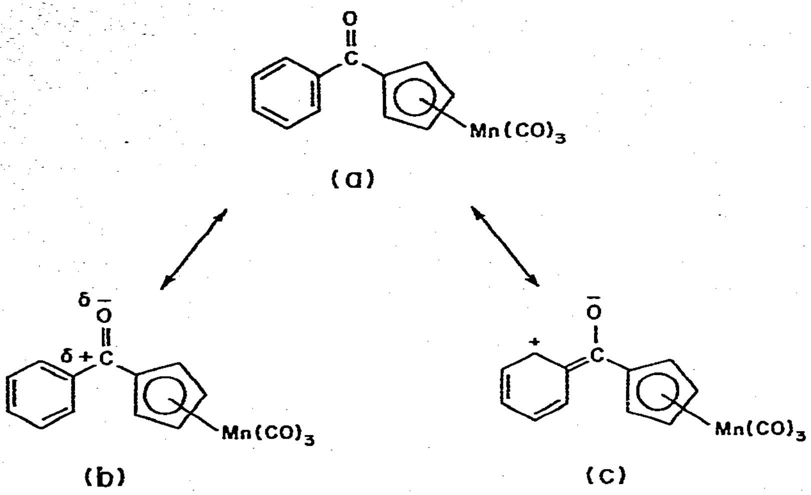


Fig. 1. Electronic effects on the structure of a (benzoylcyclopentadienyl)manganese tricarbonyl.

scribes the —$C_5H_4Mn(CO)_3$ group as being coordinated to the ketonic carbon. Such a coordination increases the electron density on the ketonic carbon thereby reducing the disparity of polarity of the C—O bond. This effect causes a decrease in the C—O bond order with concomitant decrease in ν(CO).

The phenyl ring is best considered as being conjugated to the ketonic CO (structure c), perhaps it lies more on the plane of the CO than the cyclopentadienyl ring. As a result it has a tendency to decrease ν(CO) as observed in the *para* substituted complexes. (Table 2). The higher $\nu(CO)_s$ observed for o-$CH_3C_6H_4$-$COC_5H_4Mn(CO)_3$ are perhaps due to steric effects which subsequently tend to reduce the conjugation of the ring and the carbonyl group. It does appear that the substituents on the phenyl ring decreases the $\nu(CO)_s$ in the order, o-Cl > o-F ~ o-CH_3 > H ~ m-F > m-CH_3 ~ p-Cl ~ p-F ~ p-CH_3 > p-OMe.

Ultraviolet spectra

The assignment of bands in relatively large organometallic compounds such as are described here is difficult. Lundquist and Cais [13] studied a number of organometallic carbonyl complexes and made some tentative assignments. They assigned the bands in Mn—CO complexes between 325 nm and 350 nm to Mn—C charge transfer transactions. The bathochromic shift of the band from 331 nm in (acetylcyclopentadienyl)manganese tricarbonyl to 344 nm in (benzoylcyclopentadienyl)manganese tricarbonyl is ascribed to the conjugative effect of the benzoyl group on the cyclopentadienyl ring. In this study it is observed that the magnitude of the bathochromic shift increases with increase in conjugative effect of the substituents on the cyclopentadienyl ring. However, substituents on the arene ring do not seem to have significant effects on this band. This confirms the results obtained from the infrared studies, that substituents on the arene ring do not seem to have significant effects on the electronic environment of the CO's of the $Mn(CO)_3$ group.

A striking feature of the spectra is the sensitivity of the band around 250 nm to changes of substituents at the *para* position of the arene ring. This band

TABLE 4

ULTRAVIOLET SPECTRAL DATA OF $XC_5H_3(Y)Mn(CO)_3$

X	Y = H		Y = α-CH_3		Y = β-CH_3	
	nm	$\epsilon_{max}(10^3)$	nm	$\epsilon_{max}(10^3)$	nm	$\epsilon_{max}(10^3)$
H	331	0.86	331	1.15		
	216	11.6	216	8.82		
C_6H_5CO	344	1.75	347	1.01	345	2.03
	282	2.34	276	1.25	286(sh)	2.26
	247	14.6	245	8.57	247	13.9
	209	25.9	215	12.9	215	20.4
o-$CH_3C_6H_4CO$	337	1.62	341	1.76		
	285	4.68	280	2.68		
	243	9.80	247(sh)	10.6		
	211	23.5	213	26.4		
m-$CH_3C_6H_4CO$	339	1.58	343	2.02	410	0.46
	289	4.50	284	3.66	322	2.17
	251	11.7	248	17.9	253	5.42
	215	17.3	218	27.8	212	17.5
p-$CH_3C_6H_4CO$	339	1.97	338	2.73	338	1.99
	257	14.9	257	22.6	257	8.74
	215	22.1	213	33.9	213	13.9
o-FC_6H_4CO	342	2.00				
	278	2.87				
	239	15.8				
	216	21.9				
m-FC_6H_4CO	347	2.14	350	2.01		
	285	3.31	280	3.32		
	243	17.0	240	19.2		
	218	20.1	216	25.5		
p-FC_6H_4CO	343	1.93	342	2.40		
	294	2.12	299	2.21		
	249	1.91	249	17.1		
	213	31.8	217	21.2		
o-ClC_6H_4CO	341	1.95	345	2.02	342	1.96
	285	2.51	286	2.31	287	2.22
	238	14.5	243	17.0	244	12.1
	216	30.4	216	36.3	219	19.4
p-ClC_6H_4CO	342	21.6	348	2.11	344	2.30
	298	2.23	290	2.02	300	3.41
	257	18.1	257	20.1	256	10.0
	217	24.5	217	26.6	218	23.2
p-$OCH_3C_6H_4CO$	340	2.13	339	2.26	336	2.40
	280	15.7	280	16.6	281	17.1
	209	34.2	212	32.4	225	26.4
					213	34.5
$C_6H_5CH_2$	331	0.97	330	1.04	331	1.14
	246	12.6	223	15.6	220	16.3
	216	16.8				
$C_6H_5CH{=}CH$	284	9.51				
	212	16.1				
$C_6H_5CH_2CO$	336	1.41				
	280	2.11				
	236	7.05				
	218	12.8				

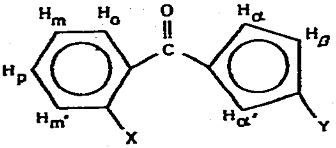
shows a bathochromic shift which appears to be of the order p-OCH$_3$ > p-Cl ~ p-CH$_3$ > p-F > p-H. The same order of bathochromic shift with changes in substituents has been observed by Doub and Vanderbelt [14] in the $\pi \rightarrow \pi^*$ transition of the aromatic ring. Moreover, it is seen (Table 4) that generally the order of decreasing bathochromic shifts of this band is *para* > *meta* > *ortho*, which is in good agreement with increasing conjugative effect on the aromatic ring. It is therefore justifiable to assign tentatively the band at around 250 nm to the $\pi \rightarrow \pi^*$ transition of the arene ring. It is noteworthy that this transition is of comparable wavelength and intensity to those of acetophenone (240 nm, $\epsilon = 13{,}000$) and benzophenone (252 nm, $\epsilon = 20{,}000$) [15].

A comparatively weak shoulder is observed between 260 nm and 310 nm in all the spectra of the ketones presently studied. They are, however, very broad and often masked by the stronger bands at shorter wavelengths. Hence it is difficult to correlate the shift of this band with substituent effects. Whether this is a $\pi \rightarrow \pi^*$ transition of the ketonic carbonyl or another Mn—C band is difficult to ascertain.

The most intense band in the spectra of these complexes is around 210 nm. This band has been observed in the spectrum of cyclopentadiene as well as in those of metal carbonyls such as M(CO)$_6$. Though Lundquist and Cais have assigned this to a M—C band, it is equally likely that this is attributed to the cyclopentadienyl ring. The fact that this band appears at the lower limits of the spectral scan where the sensitivity of the instrument is greatly reduced, makes deduction from it meaningless.

Proton NMR spectra

The positional nomenclature employed is shown below:



Whenever two protons are situated at equivalent positions with respect to the ketonic carbonyl group, a subscript is used for the proton nearer the substituent.

The α- and β-proton resonances of the monosubstituted cyclopentadienyl ring are readily assigned since the former are nearer to the electron-withdrawing carbonyl group and are therefore expected at lower fields. In cases where there is another substituent on the cyclopentadienyl ring, the corresponding α, α' and β, β' proton resonances are more difficult to assign. It is observed that a methyl group at the α-position normally results in three separate resonances attributed to the three protons of the cyclopentadienyl ring. Fig. 2 shows the cyclopentadienyl proton resonance region of the spectrum of (α-methyl-p-tolylcyclopentadienyl)manganese tricarbonyl [p-CH$_3$C$_6$H$_4$COC$_5$H$_3$(α-CH$_3$)Mn(CO)$_3$]. The doublet of doublets at τ 4.87 is assigned to the α-proton ($J(\alpha\beta) = 2.7$ Hz, $J(\alpha\beta') = 1.8$ Hz), while the triplet at τ 5.36 ppm is tentatively assigned to the β-proton ($J(\alpha\beta) = J(\beta\beta') = 2.7$ Hz). The multiplet at τ 5.24 ppm is not well resolved and is assigned to the β'-protons. This assignment is consistent with that of Shen et al. [16].

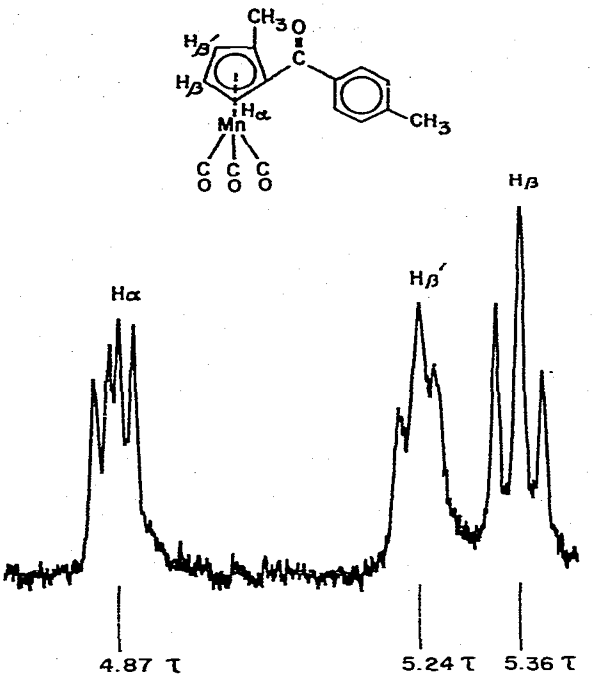


Fig. 2. The cyclopentadienyl proton resonance region of the PMR spectrum of (α-methyl-*p*-tolycyclopentadienyl)manganese tricarbonyl.

When the methyl group is substituted at the β-position of the cyclopentadienyl ring, the α and α′ proton resonances appear to coincide, making it more difficult to assign them accurately. The β proton resonance is observed at τ 5.28 ppm.

Table 5 lists the cyclopentadienyl proton resonance of the ketones. Generally, they occur at lower fields than those observed for $C_5H_5Mn(CO)_3$ (τ 5.28 ppm). This is mainly due to the withdrawal of π-electron density from the ring

TABLE 5

NMR SPECTRAL DATA OF CYCLOPENTADIENYL PROTONS OF SOME $XC_6H_4CO(Y)C_5H_3Mn(CO)_3$ COMPLEXES (τ ± 0.01 ppm)

X	Y = H		Y = α-CH_3				Y = β-CH_3			
	H_α	H_β	H_α	H_β	$H_{\beta'}$	H(Y)	H_α	$H_{\alpha'}$	H_β	H(Y)
H	4.51	5.11	4.89	5.37	5.23	7.70	4.63	4.63	5.22	7.90
o-CH_3	4.61	5.13	5.02	5.41	5.23	7.73	4.75	4.75	5.29	7.97
o-Cl	4.67	5.14	5.02	5.39	5.21	7.76	4.75	4.79	5.27	7.98
o-F	4.59	5.14								
o-OH							4.57	4.57	4.62	
m-CH_3	4.54	5.14	4.87	5.33	5.23	7.72	4.63	4.63	5.27	7.94
m-F	4.54	5.11	4.90	5.34	5.21	7.70				
p-CH_3	4.54	5.15	4.87	5.36	5.24	7.73	4.62	4.66	5.28	7.98
p-Cl	4.54	5.10	4.92	5.35	5.21	7.71	4.67	4.67	5.26	7.95
p-F	4.53	5.11					4.66	4.66	5.25	7.95
p-OCH_3	4.53	5.13	4.89	5.36	5.26	7.74	4.65	4.65	5.28	7.95

TABLE 6

NMR SPECTRAL DATA OF ARENE RING PROTONS OF SOME $XC_6H_4CO(Y)C_5H_3Mn(CO)_3$ COMPLEXES (τ ± 0,01 ppm)

X	Y = H				Y = α-CH_3				Y = β-CH_3			
	H_o	H_p	H_m	H(X)	H_o	H_p	$H_m(H_{m'})$	H(X)	H_o	H_p	$H_m(H_{m'})$	H(X)
H	2,23	2,47	2.49		2,19	2,47	2,43		2.26	2,51	2,50	
o-CH_3	multiplets at 2,73			7,59	multiplets at 2,75			7,61	multiplets at 2,73			7,60
o-Cl	singlet at 2,62				multiplets at 2,63				multiplets at 2,63			
o-F	2,53(m)		2.80(m)									
o-OH									2,20	2,54	3.00 (3.12)	
m-CH_3	2,44(m)	2,64(m)		7,59	2,45(m)	2,65(m)			2,45(m)	2,65(m)		7,57
m-F	2,51(m)	2,61(m)	2.68(m)		2,52(m)	2,62(m)	2.70(m)					
p-CH_3	2,32		2.76	7.60	2,28		2,72	7,59	2,33		2,76	7,60
p-Cl	2,28		2,58		2,31		2,59		2,31		2,59	
p-F	2,19		2.87						2,22		2,89	
p-OCH_3	2,18		3.06	6,15	2,19		3,07	6.14	2,20		3,07	6,15

by the carbonyl substituent. The deshielding effect appears to be more pronounced at the α-positions of the cyclopentadienyl ring. The chemical shift observed for $C_5H_5Mn(CO)_3$ protons (τ 5.28) in $CDCl_3$ is very much higher than the value τ 5.04 ppm observed by Shen et al. [16] in DMSO. The difference is probably due to the strong proton-accepting property of DMSO.

The cyclopentadienyl protons are apparently not affected by substituents at the *meta* and *para* positions of the phenyl ring. *Ortho* substituents tend to shift the α-proton resonance of the cyclopentadienyl ring slightly upfield, but leave the β-protons unaffected. This is perhaps due to the *ortho* substituents sterically hindering coplanarity of the π and π* orbitals of the ketonic carbonyl with the π orbitals of the arene ring. This is further supported by the methyl substituent at the α-position of the cyclopentadienyl ring which induces a further shift to higher fields of the α-protons. If the shift is assumed to be additive, then it appears that the methyl substituent at the α-position of the cyclopentadienyl ring is more effective as a steric group than the methyl at the *ortho* position of the arene ring (columns 2 and 4, Table 5). It is noteworthy that the resonances of the α-methyl protons are at lower fields than those of the β-methyl protons. Perhaps this low field shift is a result of the hyperconjugative effect of the methyl group being reduced by the π-effect of the ketonic carbonyl group.

The spectrum of $C_6H_5COC_5H_4Mn(CO)_3$ shows, apart from the two triplets at higher fields due to the cyclopentadienyl protons, a doublet of doublets centred at τ 2.23 and two triplets at about τ 2.47 ppm of intensity ratio 2/3. They are assigned as indicated and the observed coupling constants are *J*(*ortho*) = 7.5 Hz; *J*(*meta*) = 1.8 Hz.

Generally, monosubstituted benzenes having an electron-withdrawing substituent such as CO show well resolved signals. Disubstituted analogues are aften more complex except perhaps *para* disubstituted benzenes which can be analysed as AA'BB' systems [17]. In systems considered here, the *J*(*ortho*) values are very much higher than those of *J*(*meta*) and *J*(*para*). As such the *para* disubstituted benzenes approach an AB type system and have been considered accordingly.

The substituent effects on the arene proton resonances are summarised in Table 6. The arene protons in the table are named with respect to the position of the ketonic carbonyl group.

In the *para* disubstituted derivatives, the *para* substituent shifts the *ortho*

TABLE 7

NMR SPECTRAL DATA OF SOME COMPLEXES OF THE TYPE $RC_5H_4Mn(CO)_3$ (τ ± 0.005 ppm)

R	H(phenyl)	H_α	H_β	Miscellaneous
H		5.28	5.28	
C_6H_5	2.67(m)	4.83	5.24	
$C_6H_5CH_2$	2.74(s)	5.38	5.38	$H(CH_2) = 6.42$
$C_6H_5CH_2CO$	2.72(s)	4.60	5.22	$H(CH_2) = 6.12$
$C_6H_5CH_2CH(OH)$	2.75(s)	5.39	5.39	$H(CH_2) = 7.07$; $H(CH) = 8.15$; $H(OH) = 5.13$
$C_6H_5CH{=}CH$	2.67(m)	5.03	5.30	$H(CH{=}CH) = 3.19, 3.43$

(*meta* to itself) proton resonances upfield in the order, $OCH_3 > F > CH_3 \sim H \sim Cl$. The former shift is probably due to the inductive effect of the substituents while the latter can be explained by the π-electron-donating ability of the substituents. It appears that the proton resonance of the methyl protons on the arene ring are not affected regardless of the position of substitution.

The spectra of some non-conjugated systems and systems not conjugated via a ketonic CO group have also been studied. The arene proton resonance signals are usually observed as narrow multiplets, (Table 7), which suggests that the arene protons are not significantly perturbed by the substituent. The arene proton resonances of complexes with $R = C_6H_5$ and $R = CH—CHC_6H_5$ are, however, found at slightly lower field than non-conjugated substituents.

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References

1 N.J. Gogan and Z.U. Siddiqui, J. Chem. Soc. D, (1970) 284.
2 K.J. Coleman, C.S. Davies and N.J. Gogan, J. Chem. Soc. D, (1970) 1414.
3 N.J. Gogan and Z.U. Siddiqui, Can. J. Chem., 50 (1972) 720.
4 N.J. Gogan and C.S. Davies, J. Organometal. Chem., 39 (1972) 129.
5 N.J. Gogan, C.K. Chu and G.W. Gray, J. Organometal. Chem., 51 (1973) 323.
6 E.M. Doyenchuck, Ya. N. Pirig, D.K. Tolopaka, Khim. Prom. Ukr., 1 (1969) 10; Chem. Abs. 70 (1969) 275.
7 E.O. Fischer and K. Pleszke, Chem. Ber., 91 (1958) 2719.
8 P.L. Pauson, J. Amer. Chem. Soc., 76 (1954) 2187.
9 D.A. Brown and H. Sloan, J. Chem. Soc., (1962) 3849.
10 D.A. Brown and J.R. Raju, J. Chem. Soc. A, (1966) 1617.
11 D.M. Adams and A. Squire, J. Chem. Soc. A, (1970) 814.
12 L.J. Bellamy and R.J. Pace, Spectrochim. Acta., (1963) 1831.
13 R.T. Lundquist and M. Cais, J. Org. Chem., 27 (1962) 1167.
14 L. Doub and J.M. Vanderbelt, J. Amer. Chem. Soc., 77 (1955) 4535.
15 R.M. Silverstein and G.C. Bassler, Spectrometric Identification of Organic Compounds, Wiley and Sons, New York, 2nd ed., 1967 p. 165.
16 L.M.C. Shen, G.G. Long and C.G. Moreland, J. Organometal. Chem., 5 (1960) 326.
17 K.B. Wilberg and B.J. Nist, Interpretation of NMR Spectra, New York 1962 p. 317.